

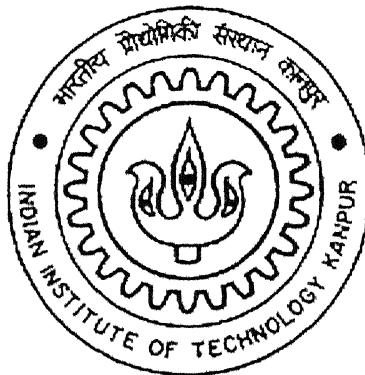
AN INVESTIGATION OF USE OF LIMESTONE AND LIGNITE FOR THE TREATMENT OF ACID MINE DRAINAGE

*A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
Master of Technology
in*

Environmental Engineering and Management

by

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**to the
DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
January, 2002**

24 APR 2002

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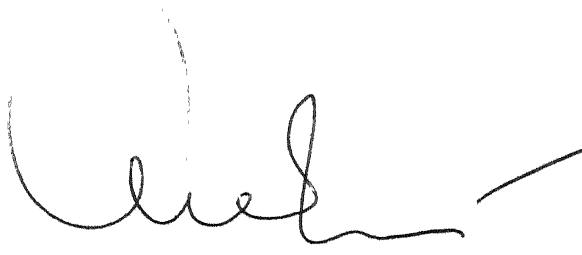
CERTIFICATE

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It is certified that the work contained in the thesis entitled "AN INVESTIGATION OF USE OF LIMESTONE AND LIGNITE FOR THE TREATMENT OF ACID MINE DRAINAGE", by Puneet Sarna, has been carried out under our supervision and that this work has not been submitted elsewhere for a degree.


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Abstract

In a laboratory study, effectiveness of limestone and lignite in treatment of Acid Mine Drainage (AMD) (pH 2.19, Al 324 mg/L, Cu 780 mg/L, Cr 318 mg/L, Co 380 mg/L, Fe 267 mg/L, Pb trace and Zn 729 mg/L) was examined. Limestone and lignite alone were not found to be effective in the treatment process; however, appreciable reduction in metal concentration and increase in pH with limestone-lignite and lime-coated lignite was observed. The study demonstrates that limestone and lignite in conjunction can be used for effective treatment of AMD. A flowsheet for subsurface treatment of AMD has been proposed.

Acknowledgements

I take this opportunity to express my sincere regards for my thesis supervisors - Prof. Dr. rer. nat. Walter Plüger (IML, RWTH-Aachen), for the encouragement and guidance he provided during my stay in Germany, and Prof. Malay Chaudhuri (IIT, Kanpur), for the patience and endurance he exhibited during my stay at IIT Kanpur. I am indeed fortunate to get an opportunity of working with both of them.

I am thankful to the authorities of the Deutscher Akademischer Austauschdienst and Indian Institute of Technology, Kanpur for award of a DAAD-Sandwich Scholarship which enabled me to conduct the experimental part of the research at the IML/ Labor für Geochemie und Umweltanalytik, RWTH-Aachen.

I express my gratitude for Dr. rer. nat. Georg Houben for his day to day guidance, suggestions and help in the experimental work. I also thank Dr. Johannes Jochum, Petra Nikolay, Christiane Schroeder, Lazaro Eleuterio, Jens Koester, Gertrud Siebel and Jutta Lauscher for their help and support.

I am also indebted to my instructors, Dr. Guha, Dr. Sharma, Dr. Ghosh and Dr. Rath for their kind cooperation throughout my stay in this department. I am also grateful to Patidarji, Shuklaji and Satvatji for their help and advice in the laboratory. I am also

grateful to Mishraji, Nekramji, RB Lalji, Yadavji and Vijayji for the cooperation they extended to me.

The joyful company of my classmates and friends, Kaka, Chaman, Anubha, Mukta, Raka, Shailesh, Bhaiya, Kaki, Bhokali, Nangu, Shakal, Chaubey, Pupuni, Bama, Abhijit, Udit and Priti will always remind me of my memorable days as a student of IIT Kanpur. I will never forget the company of Jassi, Sanjeev, Punam, Sujata, Prantik, Shahrukh and Badru. I also acknowledge the affection given to me by the 2001 batch, especially, Ramania, Dhiman, Akash, Advani and Bhakti.

I express my regards to Mrs. Chaudhuri, for she was the one who endured sir and me throughout the difficult phase of my thesis. I express my respect for Marwah uncle and auntie and Sah uncle and auntie.

I do not have words to express my feelings for my parents, for they have been the source of inspiration to me. I am what I AM just because of them.

Last but not the least I wish to thank Shiva for being with me.

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1 INTRODUCTION

The mining sector, termed as one of the basic sectors and at par with the agricultural sector in the economics of development, has been ridden with environmental problems from the very beginning. A typical mine has numerous environmental hazards associated with it, such as acid mine drainage (AMD), disposal of overburden, subsidence, mine fires and abandoned and discontinued facilities.

Most of these problems can be tackled by proper mine planning, by employing the right method of working and by altering the mining practices. The mining engineers worldwide are well equipped to deal with most of the problems, barring the AMD. The choice of appropriate mining method can minimize the production of AMD, but cannot negate it completely. Underground water is usually present in the water-bearing strata of the mining area. Apart from this, water is used extensively in mining practices to curb generation of dust, and for prevention of fire and cooling of underground operations. The water then has to be pumped out of the mine to prevent inundation. The contact of water and sulfidic ores leads to generation of AMD.

The AMD is defined as drainage flow from or caused by surface mining, underground mining or coal refuse piles that is characteristically highly acidic, with elevated levels of dissolved metals. It is characterized by low pH and increased acidity, elevated heavy metal and sulfate content, and high total dissolved solids (TDS). Depending on the composition of the mine overburden and the geological characteristics of the mining area and the geochemical composition of the seams in the near vicinity of the water-bearing strata, the pollutants released into surface and ground water can typically include any or all of the following heavy metal ions: iron, zinc, aluminum, manganese, cobalt, nickel, copper, arsenic, selenium, cadmium and lead.

Another source of AMD is the abandoned or discontinued open-pit metal-mining operations, resulting in creation of pit lakes. Depending on mineral composition of the rocks surrounding a pit, particularly the presence or absence of carbonates, water in the resulting lakes may be mildly to severely acidic, near neutral, or even alkaline (Plumlee et al, 1992). The pit water may vary greatly in pH and metal/metalloid content, and typically has high to very high sulfate concentrations (up to several thousand ppm) produced by oxidation of sulfides.

The formation of AMD is primarily a function of the geology, hydrology and mining technology employed at the mine site. A series of complex geochemical and microbial reactions occur when water is exposed to sulfidic ore minerals such as pyrite (FeS_2 , iron disulfide mineral) in coal, refuse or the overburden of a mine, producing AMD. The resulting water is usually high in acidity (if unbuffered) and dissolved metals. The metals stay dissolved in solution until the pH rises to a level where precipitation occurs (also redox potential and the concentration of other ions control metal mobility, e.g. co-precipitation of metals with iron oxides or jarosites).

Prediction of AMD is the key factor in predicting the release of dissolved metals from active and past mining operations. Within an active mining operation, the AMD can generate from a number of sources. The prerequisite for AMD is the generation of acid at a faster rate than it can be neutralized by any alkaline materials in the waste, continuous access of oxygen and water; and a rate of rainfall precipitation higher than evaporation. The most common mineral causing AMD is pyrite, but other metal sulfides also contribute. When released into the environment, AMD can lead to the disruption of aquatic ecology and there is every possibility of

heavy metals entering the food chain. Also, ferric hydroxide precipitates from AMD as reddish orange precipitate, commonly known as “yellow boy”. This destroys the esthetics of the stream into which it is discharged. The FeO_x can also clog up wells and drains.

A lot of work has been done in the field of AMD treatment and many technologies are available which can be broadly classified under active and passive treatment. While active treatment methods comprise of treating AMD with chemical compounds, passive treatment methods make use of naturally-occurring chemical and biological reactions in a controlled environment. Passive treatment methods are more popular for their ease of use and lower running costs.

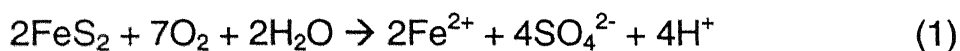
Though various treatment methods for AMD are available and are in use worldwide, there is a need to study effective and economical methods for the treatment of AMD in India. The study was aimed at providing a low-cost, easily applicable and adaptable method in terms of implementation, maintenance and simplicity. With this perspective, the study investigated the use of limestone and lignite for the treatment of AMD.

2 BACKGROUND INFORMATION

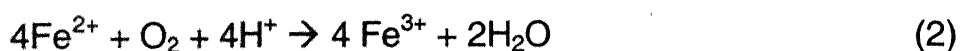
The chemical and bio-catalyzed reactions leading to the generation of AMD and the overall production of AMD in mine and impact of AMD on aquatic ecology are presented, followed by the methods of prevention and treatment of AMD. Potential of low rank coal in the treatment of AMD is also discussed.

2.1 The Chemistry of AMD

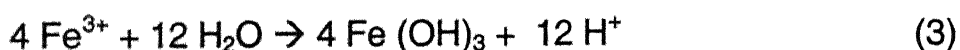
The oxidation of pyrite occurs in four steps (Kleinman et al, 1981), the first step is the oxidation of sulfide by oxygen. Sulfide is oxidized to sulfate and ferrous ion is released. This step generates two moles of acid for each mole of pyrite oxidized.



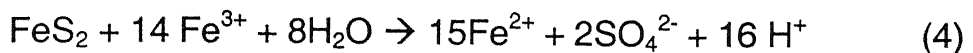
The second step involves the conversion of ferrous ion to ferric ion. The conversion of ferrous ion to ferric ion consumes one mole of acid.



The third step is the hydrolysis of iron.



The fourth step is the oxidation of additional pyrite by the ferric ion generated in step 2. This is the cyclic and self propagating part of the overall reaction, takes place very rapidly, and continues until either ferric ion or pyrite is depleted.



There are three stages in the oxidation process:

1. pH above 4.5; high sulfate and low iron concentrations, with little or no acidity. Reaction (1) proceeds both abiotically and by direct bacterial oxidation. Reaction (2) is abiotical and slows down with decreasing pH.

2. pH between 2.5 and 4.5; high sulfate, increased acidity and iron concentrations. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is still low. Reaction (1) proceeds both abiotically and by direct bacterial oxidation. Reaction (2) is predominantly determined by the activity of *Thiobacillus ferro-oxidans*.

3. pH below 2.5; high sulfate and iron concentrations. The ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ is high. Reaction (3) is totally determined by bacterial oxidation. Reaction (4) is determined by the rate of reaction (3). The rate determining step in this whole sequence is the formation of Fe (III) (Singer and Stumm, 1970).

The overall scheme of the above reaction steps proposed by Singer and Stumm (1970) and Stumm and Morgan (1970), is shown in Figure 2.1. The model bears hallmarks of electron-transfer processes in biochemical systems (Temple and Delchamps, 1953).

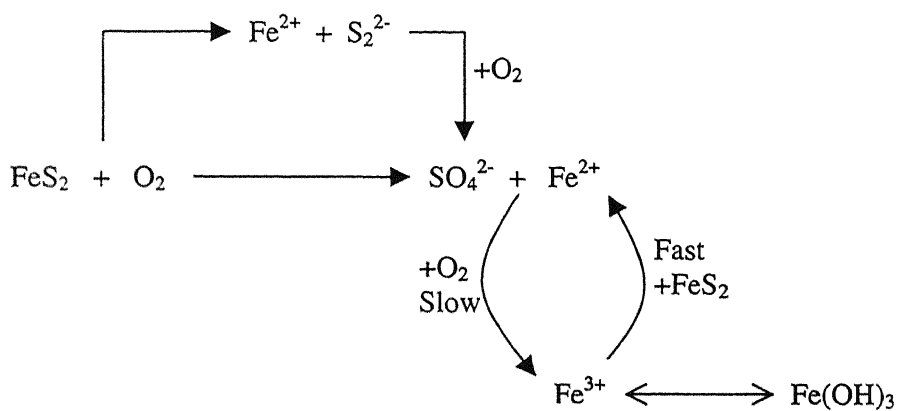


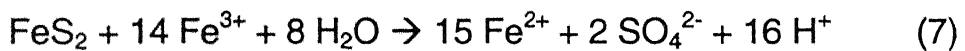
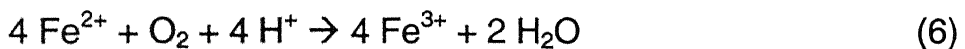
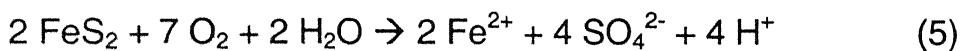
Figure 2.1 Scheme of Reactions in AMD Generation from Pyrite

2.2 Biological Influences on Chemistry of AMD

The presence of acid tolerant bacteria (*T. ferro-oxidans*) speeds up the process of sulfide oxidation. This microbe has been implicated as the major culprit in the pollution of streams emanating from active and abandoned mining operations. Abiotic oxidation of pyrite is slow. *T. ferro-oxidans* catalyzes (at a factor of 10^6) the oxidation of FeS_2 , producing ferric ions and protons. *T. ferro-oxidans* is also recognized as being responsible for the oxidation of iron and inorganic sulfur compounds in mine tailings

and coal deposits where these compounds are abundant. *T. ferro-oxidans* is acidophilic and has a physiology well suited for growth in the mining environment.

Pyritic mine tailings leach AMD originating in large part due to the metabolic activity of *T. ferro-oxidans*, which catalyzes reactions (5) and (6). This increases the rate of chemical weathering of the mine tailings. Product from the bio-catalyzed reactions (5) and (6) contribute to reaction (7), which is abiotic.

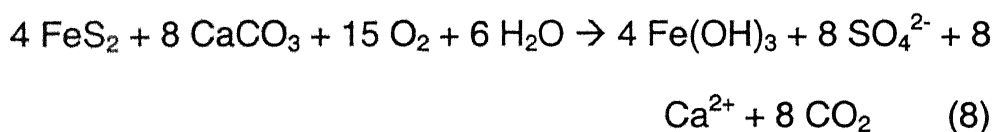


2.3 Acid Producing Potential of a Mine

The three stages discussed in section 2.1 are the primary factors, directly involved in the acid production process (Ferguson and Erickson, 1988). Reactions (1) to (4) assume that the mineral oxidized is pyrite and the oxidant is oxygen. Other sulfide minerals such as pyrrhotite and chalcocite are also amenable to oxidation and acid generation. However, research on these is limited. The intensity of acid generation by these primary factors is determined by chemical parameters such as pH (dependant on propagation of

AMD generation itself), temperature, oxygen availability (open systems) and concentration in the gas and water phase, chemical activity of iron (III), and surface area of exposed metal sulfides. Biological parameters involved include biological activation energy, population density of bacteria, rate of bacterial growth, and supply of nutrients.

The secondary factors control the consumption and alteration of the products from acid generation reactions. Neutralization of AMD can occur when carbonate minerals are present. In tailing deposits, some CaO is always left from metal extraction process and it can neutralize AMD. The combined reaction of acid generation by pyrite oxidation and neutralization of acid by calcium carbonate can be described as (Williams et al, 1982) :



The reaction shows that two moles of calcium carbonate are necessary to neutralize the acid produced by one mole of pyrite. However, the total amount of carbonate is often not available as the precipitation of iron hydroxide and calcium sulfate can armor the particles and prevent further neutralization (but can also coat

pyrite grains). Neutralization by carbonates is a relatively fast process and provides short-term buffering capacity. Acid is also consumed through reactions with silicate material providing long-term buffering capacity.

The tertiary factors producing and controlling AMD are the physical aspects of the waste materials that influence acid production, migration and consumption. The physical characteristics of mine waste and hydrological factors at the site determine the intensity of the acid generation. Oxygen advection and diffusion are affected by coarse-grained waste, which results in high production of acid (layers of high hydraulic permeability are preferred AMD sources due to enhanced pyrite accessibility). Fine-grained material limits oxygen transport and diffusion and though they have a high surface area, the oxygen availability may be limiting. The modification of secondary and tertiary factors can be looked on as ways of arriving at geochemical engineering approaches to prevent AMD.

The development of AMD with time depends on the amount and nature of acid-consuming minerals in the waste dump. The stepwise drop in pH, with periods of constant pH, is shown in Figure 2.2 (Salomons, 1995).

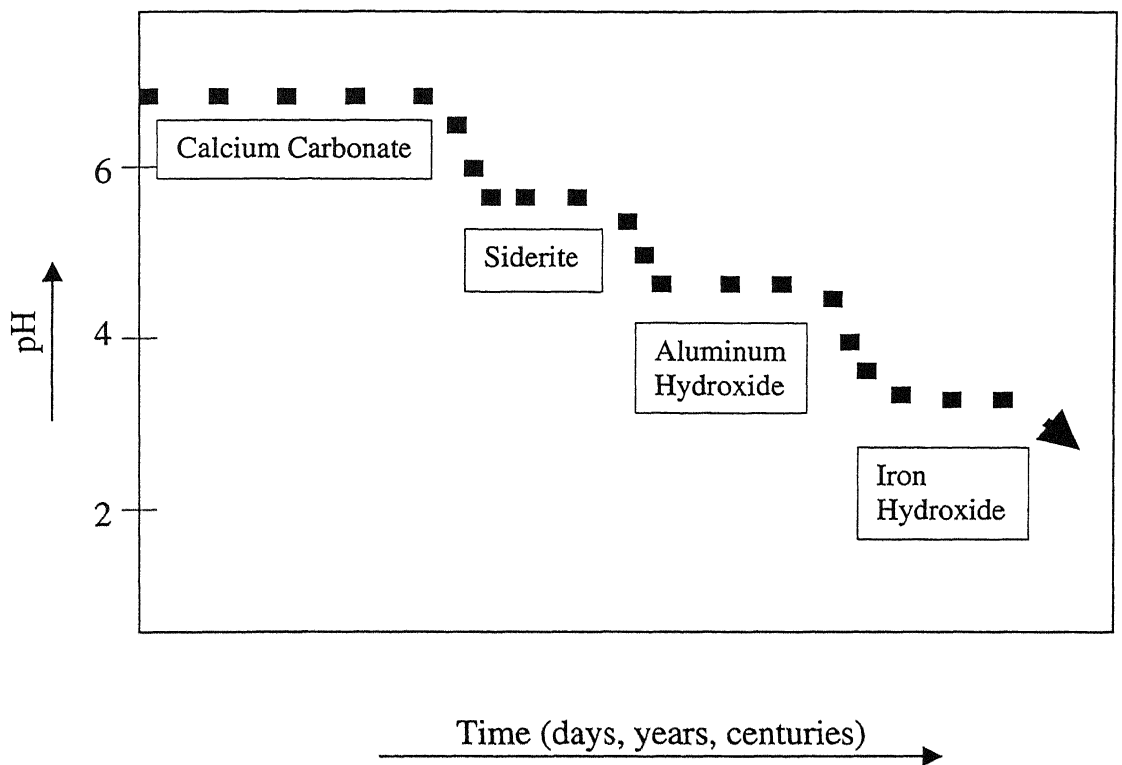


Figure 2.2 Stepwise Consumption of Buffering Capacity in a Hypothetical Waste Deposit (Salomons, 1995).

The initiation of AMD can be fast and dumps may start leaching AMD within one year. Conditions of high rainfall, such as in the tropics, are favorable for the production of AMD. Several test procedures are available for predicting AMD. Ideally, they consist of three steps – static tests, kinetic tests and mathematical modelling (Lapakko, 1992; Ferguson and Erickson, 1988; Robertson and Kirsten, 1989).

The static and kinetic geochemical tests are based on the assumption that geochemical reactions are the main factors that

control AMD quality. The static tests in use determine pyrite content or total sulfur content to calculate the potential acidity. Titration procedures are used to determine the acid-consuming ability (base potential). The net base (net neutralization) potential is calculated by subtracting the acid potential from the base potential. The acid producing potential in a rock is tied directly to the amount of sulfides bound up in the rock in various forms. Sulfides are crystalline substances that contain sulfur combined with a metal or non-metal, but no oxygen. The most common forms are pyrite and marcasite (FeS_2). Other forms include $\text{Fe}_{1-x}\text{S}_x$, Fe_3S_4 , FeS , CuFeS , ZnS , PbS , HgS , CoAsS etc. The static tests, however, do not provide information on the time scales involved. Geochemical kinetic tests study weathering under laboratory conditions or under *in situ* conditions in order to confirm the potential for generation of net acidity, and to determine the rates of acid generation, sulfide oxidation, neutralization and metal depletion. Several tests are available which simulate some, or a combination, of the processes involved in AMD (Robertson and Kirsten, 1989; Hutchinson and Ellison, 1992). Testing involves leaching of representative samples and monitoring water quality over a period of months or years under laboratory or field conditions.

Although the basic chemical and biochemical processes involved in the production of AMD and heavy metal behaviour are well known, application of this knowledge to actual field conditions is still beset with uncertainties. The combination of hydrological, biochemical, chemical and physical processes in actual waste dumps makes predictions during and after mining still a “moving target” (Salomons, 1995).

2.4 Impact of AMD on Aquatic Ecology

Once AMD is released into the streams, the heavy metals can be transported considerable distance downstream (Axtmann and Luoma, 1991). However, several physical and chemical processes operating in a stream can give rise, directly or indirectly, to attenuation of pollutants (Salomons, 1995). Metals released by the AMD are hydrolyzed when the pH increases due to dilution by receiving streams, resulting in precipitation of metals on the stream substrate. While precipitated metals adsorbed to sediment particles are carried downstream, potentially contributing to bioaccumulation by aquatic organisms, the dissolved and hydrolyzed metals in the process of forming precipitates cause acute toxicity downstream of the confluence of the acidic tributary. The aquatic communities are significantly impacted by AMD in

neutral waters below acidic tributaries by the above naturally-occurring processes (Soucek et al, 2000).

2.5 Prevention of AMD

AMD can be prevented by controlling the access of oxygen to the acid-generating deposits. A very efficient way is to flood the waste deposits to prevent access of oxygen, but this method is subject to local geological conditions. Other measures include covering with alternating layers of material (clay, gravel, and topsoil) and a final revegetation programme to prevent erosion. Use of bactericides have been investigated. They are able to slow down the microbial processes; however, they do not last as they are subject to degradation (and repopulation by bacteria is common). Measures taken after the end of mine life are expensive, as is illustrated by the cases of Rum Jungle mine site in Australia (Harries and Ritchie, 1988) and Clark Fork river system (Axtmann and Luoma, 1991; Moore and Luoma, 1990). Measures performed during mine life are more effective. They depend on local circumstances, such as available space, nature of waste materials and hydrology and sensitivity of the surroundings to impact.

2.6 Treatment of AMD

The treatment of AMD can be classified into two categories, namely, active treatment methods (chemical treatment) and passive treatment methods. The control of acid generation can be achieved by removing one or more of the three essential components in acid-generating process i.e., sulfide, air, or water. Steps that can be taken to control AMD include waste segregation and blending, base additives, covers and caps, bactericides, and collection and treatment of contaminants

2.6.1 Active Treatment Methods – Chemical Treatment

The treatment system chosen for a particular site usually incorporates a chemical treatment system to neutralize AMD. The chemicals commonly used are calcium carbonate, calcium hydroxide, calcium oxide, sodium carbonate and sodium hydroxide. The goal of the treatment system is to allow chemicals to combine with the mineral acidity so as to precipitate the metals out of the AMD. This neutralizes the effluent so that it can be released without causing harm to the environment. The drawback of this system is the high cost of chemicals and wages for operators, installations, construction thereof, etc. In addition, they produce difficult-to-dewater sludges and sometimes the chemicals may not react completely, producing high volumes of sludge.

An alternative chemical that solves many of the above problems is anhydrous ammonia. It is inexpensive, produces good sludge and reacts quickly and completely. However, it is dangerous to handle and can be toxic to the aquatic life in unionized form. Also, it has a potential to be nitrified (and thus cause algae blooms) by bacteria and increase acidity downstream.

2.6.2 Passive Treatment Methods

The concept of passive treatment is to allow the naturally-occurring chemical and biological reactions that aid in AMD treatment to occur in the controlled environment of the treatment system, and not in the receiving water body. Passive treatment conceptually offers many advantages over conventional active treatment systems. The use of chemicals and energy consuming treatment processes is virtually eliminated with passive treatment. In addition, the operation and maintenance requirements of passive treatment systems are considerably less than active treatment systems. Designing a passive treatment system requires the understanding of mine water chemistry, available treatment techniques and experience. Analytical sampling of the AMD is extremely important in the selection of appropriate treatment technology.

2.6.2.1 Compost or Anaerobic Wetlands

Compost wetlands or anaerobic wetlands as they are sometimes called, consist of a large pond with a lower layer of organic substrate. The flow is horizontal within the substrate layer of the basin. Typically, the compost layer is made from spent mushroom compost that contains about 10 percent calcium carbonate. Other compost materials include peat moss, wood chips, sawdust or hay (Gazea et al, 1996). The compost wetland acts as a reducing wetland where the organic substrate promotes chemical and microbial processes that generate alkalinity and increase the pH. The compost removes any oxygen in the system. This allows sulfate to be reduced and keeps the metals from oxidizing and armoring or coating the limestone present in the compost. Microbial respiration within the organic substrate reduces sulfates to water and hydrogen sulfide, and metals precipitate as metal sulfides. The anoxic environment within the substrate also increases the dissolution of limestone (Hellier, 1996).

2.6.2.2 Diversion Wells

Diversion wells are another simple way of adding alkalinity to acidic waters. Acidic water is conveyed by a pipe to a downstream well which contains crushed limestone aggregate. The hydraulic force of pipe flow causes the limestone to turbulently mix and

abrade into fine particles and prevent armoring. The water flows upward and overflows the well where it is diverted back into the stream. Diversion wells require frequent refilling with clean limestone to assure continued treatment.

2.6.2.3 Open Limestone Channels

Open limestone channels are the simplest passive treatment method. Open limestone channels are constructed in two ways. In the first method, a drainage ditch is constructed of limestone and AMD-contaminated water is collected by the ditch. The other method consists of placing limestone fragments directly in a contaminated stream. Dissolution of limestone adds alkalinity to the water and raises the pH.

2.6.2.4 Anoxic Limestone Drains (ALD)

An anoxic limestone drain (ALD) is a buried bed of limestone constructed to intercept subsurface mine water flows and prevent contact with atmospheric oxygen. Keeping oxygen out of the water prevents oxidation of metals (especially Fe^{2+}) and thus the armoring of limestone. The sole purpose of ALD is to provide alkalinity, thereby changing net acid into net alkaline water (Gazea et al, 1996).

2.7 Potential of Low Rank Coals in Treatment of AMD

Low rank coals (brown coal and lignite) and other related cellulosic materials can be used for extraction of metals from AMD. The chemical structure of these materials include carboxylic acid (COOH) and phenolic hydroxyl (OH) functional groups, and it has been shown that the hydrogen of these groups is capable of ion exchange with calcium and barium (Schafer, 1970). Coals are especially favorable because of their high surface area. Peat and wood sawdust can be used in the same way as low rank coals (Siviour et al, 1971). The functional groups capable of ion exchange with metals are also contained in peat (Coupal and Lalancette, 1976) and in wood (McGinniss and Shafizadeh, 1980).

The low rank coals have been used for metal wining from solution, ranging from weakly acidic to slightly alkaline (Wesolowski and Ryzczek, 1965; Ong and Swanson, 1966) and ammonical solutions (Siviour et al, 1971; Cullen et al, 1972; Altekar et al, 1974; Saha et al, 1977; Cullen et al, 1978; Cullen and Siviour, 1981). Ion exchange media produced by contacting brown coal, lignite, peat or wood sawdust with an aqueous slurry of lime, were shown to be effective in treating metal containing solutions and in extracting copper, nickel, chromium, cadmium, lead, zinc,

mercury, cobalt, silver, iron, manganese, vanadium, germanium, gallium, aluminum, antimony and uranium (Cullen and Siviour, 1982).

3 SCOPE OF THE STUDY

AMD or water contaminated with AMD poses a problem to aquatic life, and it is not acceptable from an esthetic point of view. It becomes essential to treat AMD before it is discharged to a natural water body. Various treatment methods utilizing chemical compounds and naturally-occurring chemical and biological reactions are available.

In order to find a low-cost and effective method for the treatment of AMD, the present study was undertaken to examine the effectiveness of limestone, lignite and lime-coated lignite as media to neutralize and remove the heavy metals from AMD and making it suitable for discharge into natural water streams.

The experimental setup was designed as an upward-flow diversion well and was aimed at achieving an efficient system with the combination of techniques and use of low-cost technology. The aim of the study necessitated use of such materials (media) which were available easily and cheaply throughout, and required minimum pre-treatment.

4 MATERIALS AND METHODS

4.1 Acid Mine Drainage

The chemical composition of AMD varies largely from site to site, the composition of heavy metals in AMD can vary from a few mg/L to few thousands mg/L. A typical composition of AMD is shown in Table 4.1 (Gazea et al, 1996; Deissmann et al, 1995).

Table 4.1 Typical Composition of AMD

Metal	Metal Content, mg/L	
	Coal Mines	Metal Mines
Fe	1 – 473	8.5 – 3200
Zn	-	0.04 – 1600
Al	1 – 58	≈ 300
Mn	1 – 130	0.4 – 1
Cu	-	0.005 – 76
Pb	-	0.02 – 90
Co	-	≈ 1.5
Cr	-	-
pH	2.6 – 6.3	2.0 – 7.9

Based on this typical composition, a synthetic AMD was prepared for the experiments. The synthetic AMD was designed as a worst-case condition with all the metals on the higher side of the typical range and, in some cases, exceeding those to take into

account the higher quantity of metals found in leaches from mine tailings ponds and other associated facilities of the mine. The synthetic AMD was prepared by dissolving crushed single crystals of pyrite in distilled water with continuous stirring. To increase the rate of oxidation, hydrogen peroxide (H_2O_2), reagent grade, was used. The pH of the solution was continuously monitored and when it stabilized to about 3, heavy metals (Fe, Al, Cu, Zn, Co, Cu and Pb) in the form of chlorides and hydroxides of reagent grade, supplied by MERCK, were added in predetermined quantities. This further reduced the pH of the solution to 2.19. The supernatant solution was then used for experiments. The chemical composition of the AMD is shown in Table 4.2. It was observed that even after

Table 4.2 Chemical Composition of AMD used in Experiments

Heavy Metal	Concentration, mg/L
Fe	267
Zn	729
Al	324
Cu	780
Co	380
Cr	318
Pb	Trace
pH	2.19

adding substantial amount of lead chloride (PbCl_2), the lead in solution was in trace amounts. This was attributed to precipitation of lead sulfate (PbSO_4 , anglesite) from the solution and was later confirmed by chemical analysis of the bottom sediment.

4.2 Limestone and Lignite

Limestone used in the experiments was sourced from the local quarries (Devonian limestone) in the vicinity of Aachen, Germany. The limestone was then crushed in the laboratory and the particle size of limestone used in the experiments was in the range 2-4 mm. Lime was prepared in the laboratory from the limestone by heating the powdered limestone in a furnace at 1000 °C.

Lignite used in the experiments was from the 6th and 7th seam (Inden and Neurath formation) of the tertiary (miocene) Rhine Valley Coal-Field, Germany. The lignite was also crushed and sieved to particle size in the range 2-4 mm.

Lime-coated lignite was prepared by soaking lignite (1964 mL) in 300 mL of lime slurry (166 g/L) overnight, followed by drying at room temperature (Cullen and Siviour, 1982).

4.3 Experimental Setup

The experimental setup consisted of airtight vertical columns, 10 cm in diameter and 25 cm long. The media were packed into the columns under wet condition. AMD was passed through the columns by means of a peristaltic pump, manufactured by BVP GmbH, to maintain a steady flow rate throughout the experiment. The columns were operated as upward-flow diversion wells. The only source of oxygen in the columns was the dissolved oxygen in the AMD. The AMD was made to flow upwards in vertical columns to expel air bubbles. The inlet to the columns were at the bottom in the center. Nylon mesh was used to divide the flow uniformly across the cross section of the columns. The effluent from the columns were passed through flow-cells where electrodes for measuring pH were deployed, to monitor the effluent pH at an interval of 20 minutes. Effluent samples were collected at regular intervals at the exit point of the columns, and analyzed for heavy metal concentration. A schematic view of the experimental setup is shown in Figure 4.1. The actual experimental setup is shown in Figure 4.2 and 4.3.

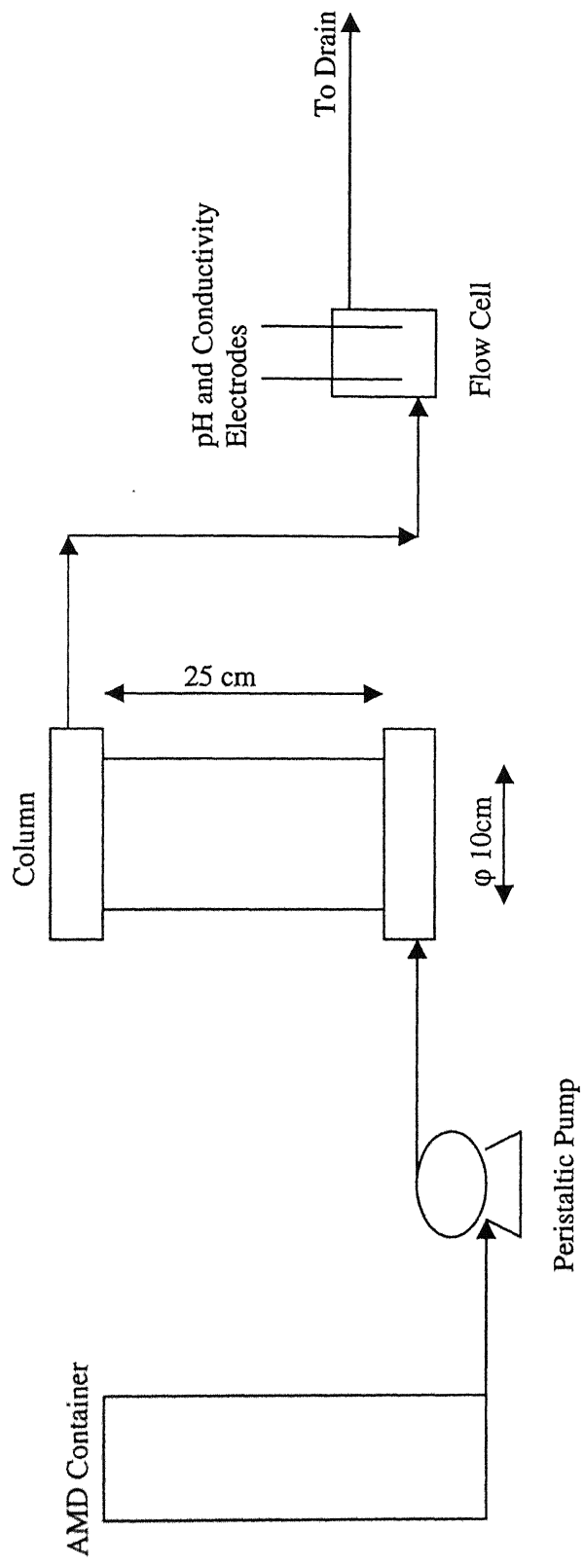


Figure 4.1 A Schematic View of the Experimenteantal Setup

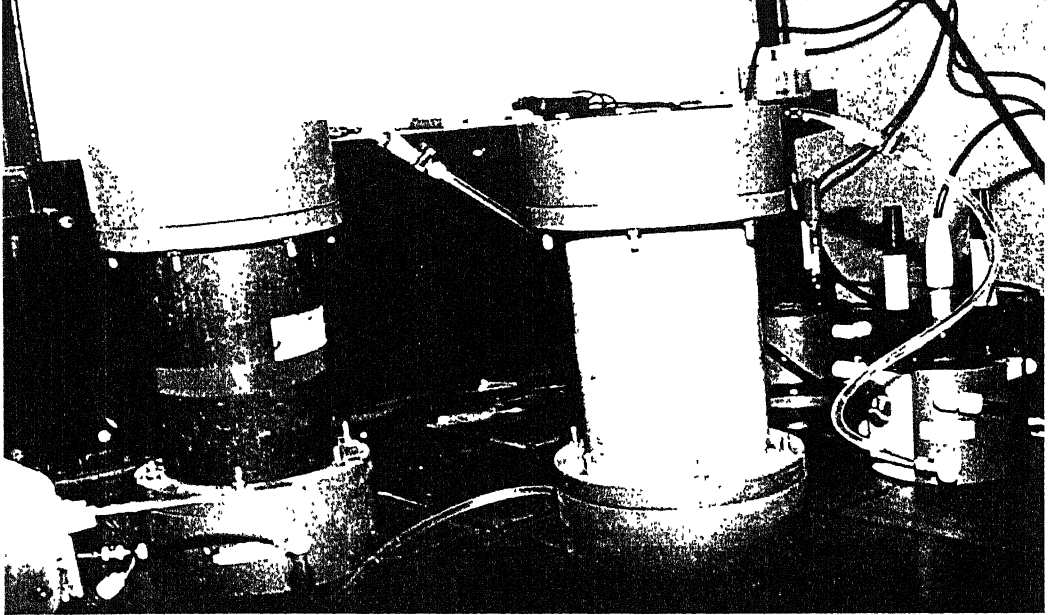


Figure 4.2 Experimental Setup

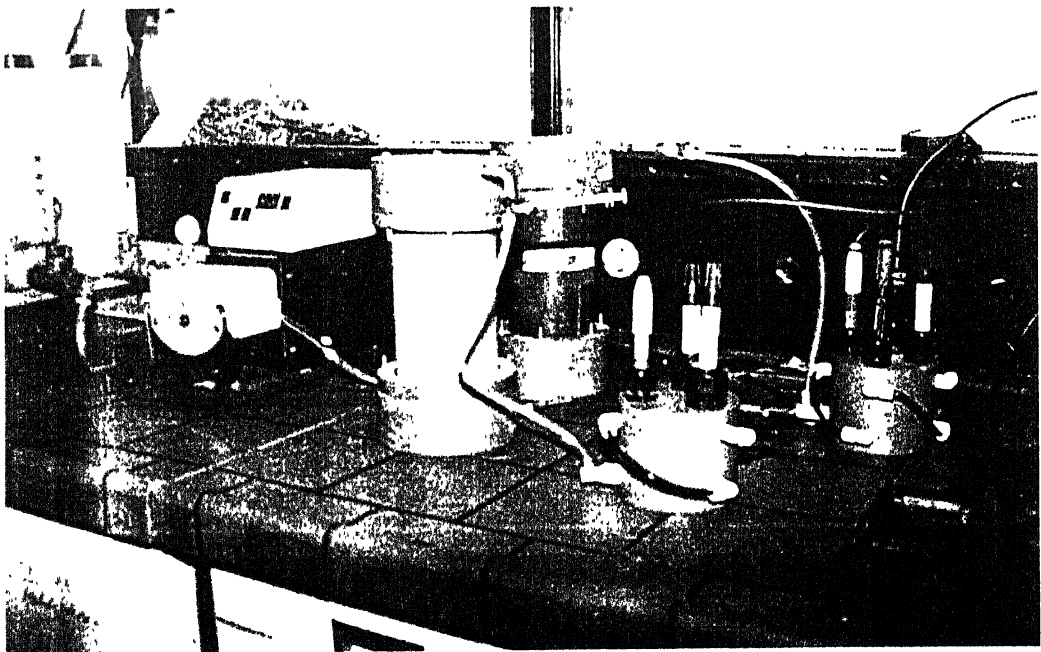


Figure 4.3 Experimental Setup (Another View)

4.4 Measurement of pH and Conductivity

The pH and conductivity of the effluent was monitored throughout the duration of the experiment by a Multiline Multiparameter P4, manufactured by M/s WTW, GmbH. SenTix 41 pH electrode and TetraCon 325 conductivity cell were used in conjunction with the P4 set. The pH and conductivity of the influent AMD was monitored once in a day. The pH electrode was calibrated twice a day using standard buffers of pH 4.1 and 7.0. The conductivity cell was calibrated once a week or before the start of a cycle of experiment.

4.5 Analysis of AMD and Effluent

The AMD and the effluent from the columns were analyzed for metal concentration using inductively coupled plasma optical spectrometry (ICP-Optical Spectrometry) on an Optima 2000 DV instrument, manufactured by M/s Perkin-Elmer.

4.6 Analysis of Media and Precipitate

Raw and spent media in the columns were analyzed for metals by x-ray diffraction (XRD) and for metal concentration by x-ray fluorescence (XRF), and the precipitates collected in the columns were analyzed by XRD.

5 RESULTS AND DISCUSSION

5.1 Column Tests

In the first batch of experiments, five columns were deployed – two columns of limestone and three columns of lignite. Two limestone columns were set up in series with two lignite columns, with lignite following limestone, and the third lignite column was run alone. A flow rate of 3.5 mL/min was maintained (empty-bed contact time 561 min). In the second batch of experiments, two columns of lime-coated lignite were deployed. Effluent samples were drawn from the exit points of limestone, limestone-lignite, lignite and lime-coated lignite columns twice a day.

5.1.1 Effluent pH

The pH of the effluent from all the columns are shown in Figure 5.1. It was observed that pH of the effluent from limestone columns was much more in the acceptable range, rather than the effluent pH of the lignite columns. Low pH of the effluent from the lignite columns was attributed to the sulfur (pyrite) content (2.479 % w/w) of the lignite used. The pH of the effluent from the limestone columns were observed to start from the order of 8 and were found to stabilize at the order of 6.3. The initial pH of the effluent from the lignite columns were of the order of 4 and

stabilized at the order of the influent pH. The initial pH of effluent from lime-coated lignite columns were of the order of 6.8 and stabilized at 3.5.

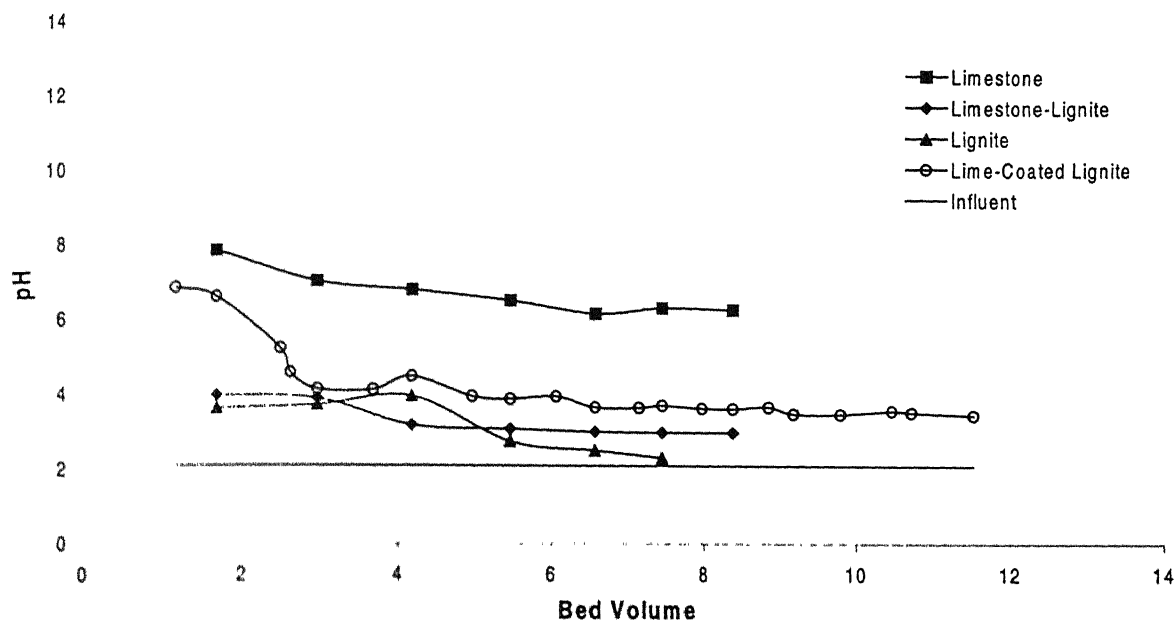


Figure 5.1 pH of Effluent

5.1.2 Metal Concentration of Effluent and Media

The metal concentrations in the effluent from the columns are shown in Figure 5.2. For the columns run in duplicate, average values are reported. The raw and spent media in the columns after the experiments were analyzed for metal content and to study mineralization, if any, in the columns. The columns were divided into 3 to 4 zones and representative samples from each zone were

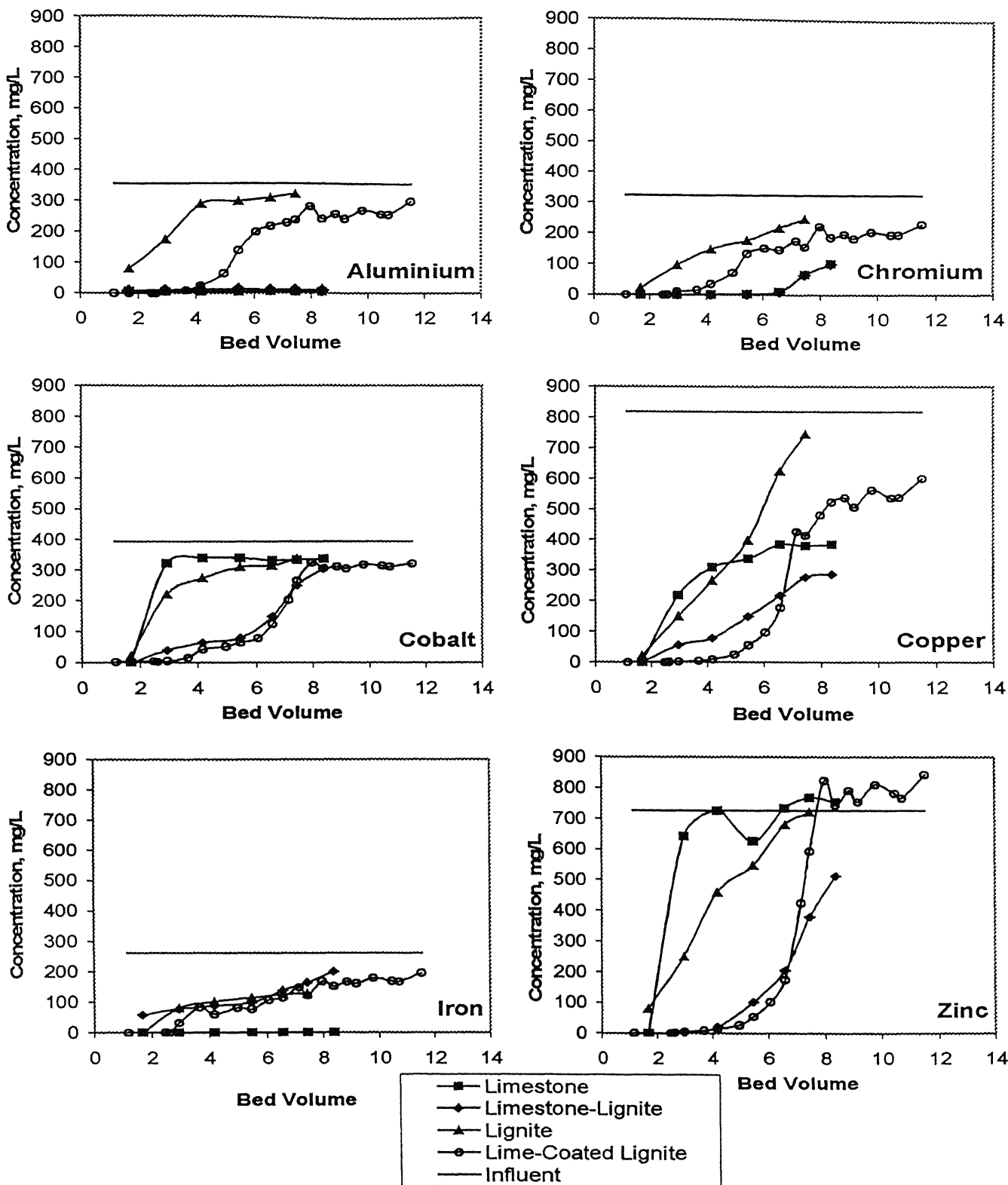


Figure 5.2 Metal Concentration in Column Effluent

analyzed. Figure 5.3 shows the zones in the columns. The metal contents of media are shown in Table 5.1. Copper, cobalt, lead and zinc were analyzed by the trace elements methods and their concentrations were obtained directly. Aluminum, chromium and iron were analyzed as oxides and the concentrations shown in Table 5.1 were suitably converted.

Amongst the media tested, limestone was most effective in removing aluminum, chromium and iron from the AMD, apparently by precipitation at high pH (Cravotta and Trahan, 1999). The hydrous oxides of aluminum and iron were visible as loosely bound orange-yellow coatings on spent limestone. The accumulation of hydrous oxides and elevated pH promoted coprecipitation of dissolved chromium.

Lignite removes metals by adsorption which is mainly physical on its surface and chemical on the carboxylic and phenolic groups of its humic acid (Xia, 1985). Cobalt adsorption is maximum in the pH range 8-9 (Nathsarma and Sarma, 1992, Saha et al, 1977), while copper and zinc adsorption occurs in the pH range 4-5 (Karabulut et al 2000). Lignite alone was not very effective in removing any of the

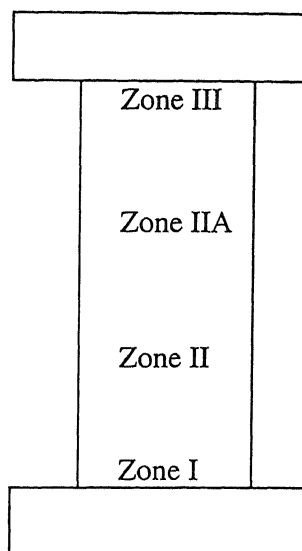


Figure 5.3 Sampling Zones in a Column

Table 5.1 Metal Content of Media

Column	Zone	Al	Cr	Co	Cu	Fe	Zn	Pb
Limestone	Raw	794	ND	ND	ND	1748	Trace	ND
	I	4285	4399	58	942	4056	351	508
	II	159	513	35	456	1608	294	54
	III	529	41	16	532	1258	249	16
Lignite (after Limestone)	Raw	10793	ND	ND	ND	187832	ND	5
	I	12379	260	1868	3518	85594	5835	19
	II	13092	123	1479	2564	118322	4129	10
	III	13807	82	1175	2235	90979	3401	11
Lignite	Raw	10793	ND	ND	ND	187832	ND	5
	I	13317	290	1208	2796	84266	2697	251
	II	11978	145	853	1806	81189	2329	36
	III	11015	072	658	1569	102187	2192	22
Lime- coated lignite	Raw	ND	ND	ND	ND	127919	ND	16
	I	794	480	2498	5678	111748	4321	855
	II	18865	346	2316	4569	95681	3965	556
	IIA	16195	257	2165	4236	125288	3846	177
	III	11478	112	2291	3967	80114	3796	135

All values in ppm. Al, Cr and Fe were measured as oxides. ND = Not Detected

metals as the pH in the lignite column was in the range of 2-4 (Figure 5.1). However, lignite following limestone (limestone-lignite) removed cobalt, copper and zinc that escaped through the limestone column, but released some iron into the effluent by oxidation of its own pyrite content. The influent pH of the lignite column following limestone was in the range suitable for cobalt adsorption (Figure 5.1), and then the sulfur content (pyrite) of lignite decreased the pH of the solution resulting in copper and zinc adsorption. Lime-coated lignite was as effective as limestone-lignite in removing cobalt, copper and zinc; however, showed early breakthrough for aluminum and chromium, apparently due to less lime available in lime-coated lignite medium compared to that in limestone-lignite media.

Metal content of the spent media in comparison with the raw media (Table 5.1) supports the above inferences. Lead was observed in the spent limestone, lignite and lime-coated-lignite, but not in the effluent as it was removed completely by the media. Further, mineralization of iron was observed in the limestone columns. The iron oxides were found to armor limestone, but when lignite and lime were present together, no mineralization was observed.

The bed volumes treated in the experiments were on the lower side as the AMD used was designed as a worst-case condition. However, the study has established the usefulness of limestone – lignite combination for treatment of AMD.

5.2 Practical Application

The suitability of this method of treatment of AMD for mining application would depend on many factors which include the residual heavy metal concentration, residual pH, availability and cost of limestone/lime, lignite and other forms of low rank coals at the mining site.

Based on the results of study, the best treatment method would be a diversion well with a limestone-lignite or lime-coated lignite bed. However, a limestone-lignite bed may be more economical as that would save on the cost of lime coating of lignite.

For areas where available lignite also contains some sulfur, it would be advisable to use a limestone bed above the limestone-lignite bed as post treatment to raise the pH of the effluent before it is discharged into the natural surroundings. A schematic flow sheet for subsurface treatment of AMD is shown in Figure 5.4. Bench-

scale experiments with actual AMD, limestone and lignite need to be carried out for design of treatment system.

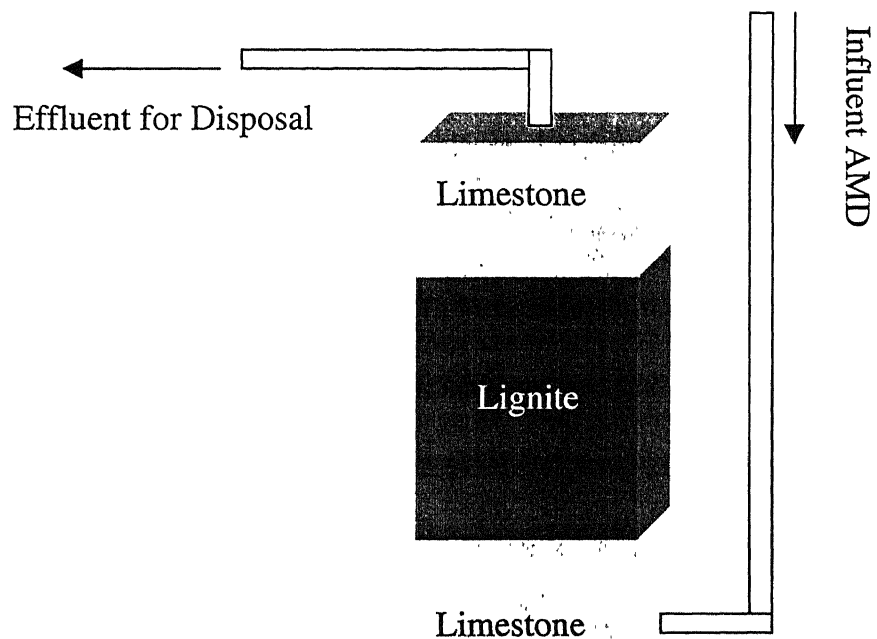


Figure 5.4 Subsurface Treatment of AMD

6 SUMMARY AND SUGGESTIONS FOR FURTHER WORK

6.1 Summary

An investigation of use of limestone and lignite for the treatment of a synthetic AMD (pH 2.19, Al 324 mg/L, Cu 780 mg/L, Cr 318 mg/L, Co 380 mg/L, Fe 267 mg/L, Pb trace and Zn 729 mg/L) was conducted. Limestone and lignite alone were not effective as treatment media; however, appreciable reduction in metal concentration in the effluent was achieved with limestone-lignite and lime-coated lignite. The pH of the effluent from limestone beds was in the near neutral to alkaline range, while the pH of the effluent from the lignite beds was in the acidic range, because of the sulfur content of lignite. The study demonstrated that a limestone-lignite bed or a lime-coated lignite bed could be used for effective treatment of AMD. A flow sheet for treatment of AMD was proposed.

6.2 Scope for Further Work

The study was conducted in Germany with the use of German lignite and limestone, German lignite has more pyrite content than Indian lignite. This limits the applicability of the study directly to Indian conditions, hence a study with Indian coal and

other raw material should be carried out. Also, there is a need to further experiment with different amounts of lime coating on lignite to achieve the optimum level under Indian conditions. Experiments need to be carried out with actual AMD for establishing a relationship between metal content, type of lignite used and amount of lignite required.

A cost benefit analysis of using lime-coated lignite and limestone-lignite needs to be conducted to determine which method would be more economical in the long run.

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